A Specific Cation Stabilization Parameter for the Linear Correlation of Relative Oxidation Potentials

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A specific cation stabilization parameter based on electrochemical oxidation potential differences within a family of similar electron donors can be used to explain unexpected relative oxidation potentials.

We reported recently that bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF or 'BEDO') has a higher oxidation potential than tetrathiafulvalene (TTF) even though it has resonance electron releasing substituents.[1] In the meantime it has been determined, in the gas phase (UVPES), that BEDO has a lower ionization potential than TTF.[2] Hypothetically, the ease of oxidation of an electron donor should be a function of the polarity of the medium; thus, the relative ionization potential of BEDO *vs.* TTF, expressed as [E1(BEDO) − E1(TTF), ΔE1] should be a function of the polarity of the solvent/electrolyte system. However, plots of ΔE1 *vs.* the solvent's dielectric constant (ε), the empirical parameter[3] E_T, the Kirkwood (ε − 1)/(2ε + 1) relation,[4] or the Taft π^* parameter[4] (Figure 1) showed essentially no correlation. Further exploration led us to discover that the difference between the potentials of the first and second oxidation steps [E2 − E1, ΔE] of BEDO, TTF, and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is an excellent measure of stabilization of stable thiafulvenoid radical cations and dications by the solvent/electrolyte combination.

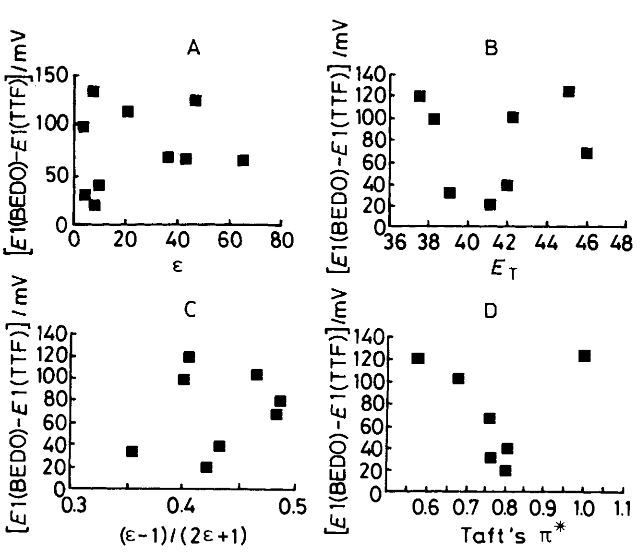

Figure 1. Plots of the difference between the first oxidation potential of BEDO and TTF *vs.* (A) the dielectric constant of the solvent, (B) the parameter E_T, (C) the Kirkwood relation, (D) the Taft π^* parameter. The oxidation potentials for this and the remaining figures were determined by cyclic voltammetry *vs.* Ag/Ag$^+$ using Bu_4NPF_6 (0.1 M) as electrolyte.

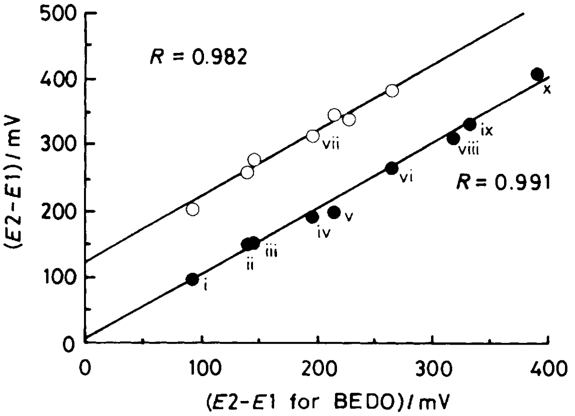

Figure 2. Plots of the difference between the first and second oxidation potentials of TTF (○) and BEDT (●) *vs.* the difference in oxidation potential of the two oxidation states of BEDO. *R* represents the linear correlation coefficient.

Solvents: i, DMSO; ii, THF; iii, 1,2-dimethyloxyethane; iv, sulpholane; v, acetone; vi, acetonitrile; vii, propylene carbonate; viii, chloroform; ix, 1,2-dichloroethane; x, methylene chloride.

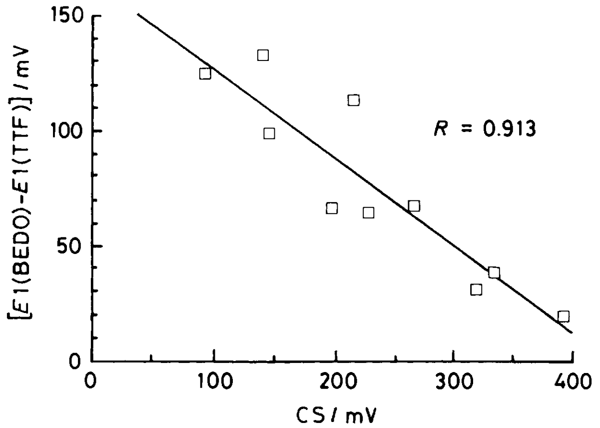

Figure 3. Plot of the difference between the first oxidation potential of BEDO and TTF *vs.* CS (E2 − E1 of BEDO). *R* represents the linear correlation coefficient.

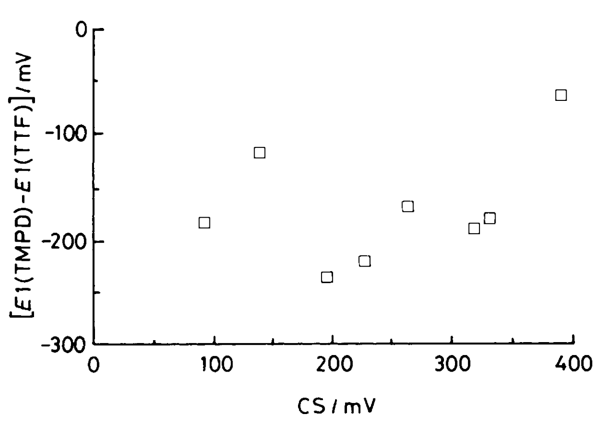

Figure 4. Plot of the difference between the first oxidation potential of TMPD and TTF *vs.* CS.

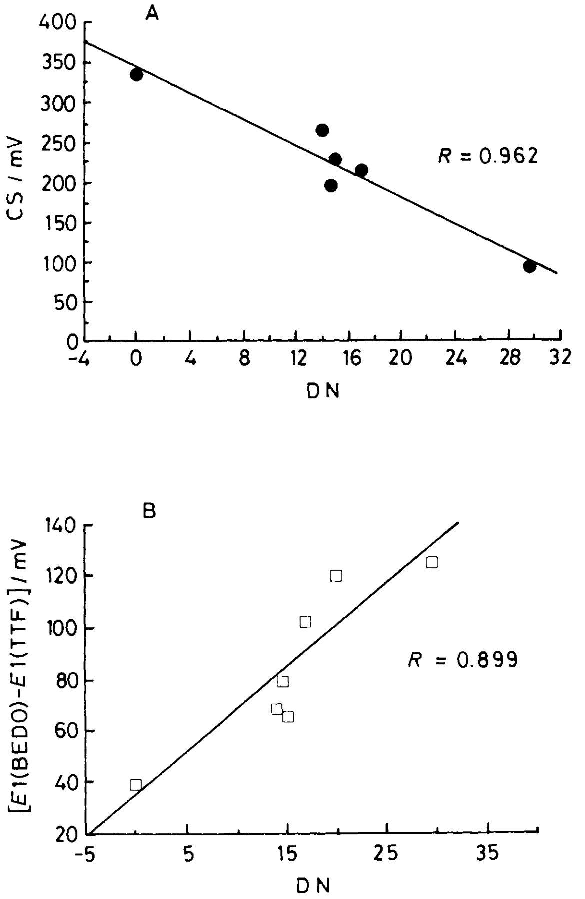

Figure 5. (A) Plot of CS *vs.* DN. (B) Plot of the difference between the first oxidation potential of BEDO and TTF *vs.* DN. *R* represents the linear correlation coefficient.

In the above attempts to correlate $\Delta E1$ with various solvent parameters, the following important observations were made. (i) In all solvent/electrolyte systems BEDO is oxidized at higher potentials compared with TTF. (ii) In the case of the ethers, 1,2-dimethoxyethane and tetrahydrofuran (THF), relatively large values for the potential difference $\Delta E1$ were accompanied by relatively small values for the voltage separation of the two oxidation steps ($E2 - E1$, ΔE) for all three compounds. In contrast, in the three halogenated solvents investigated, small values for $\Delta E1$ corresponded to large values for the respective potential separations, ΔE. (iii) Large ΔE occurred in solvents with small Gutmann DN[5,6] (solvent donicity) numbers and, conversely, small ΔE values were observed in solvents with large DN numbers (see Figure 5A).

In the DN scheme, the solvents are classified as electron pair donors, DN being defined as the negative enthalpy of the reaction between the solvent and antimony pentachloride. The ether solvents (THF and 1,2-dimethoxyethane) and dimethyl sulphoxide (DMSO), having high donor numbers, rank above acetone and acetonitrile, which in turn rank above the chlorinated solvents, with 1,2-dichloroethane having a DN ≈ 0.

Since the effect of the supporting electrolyte is not considered in the Gutmann scale or any other solvent parameter, we tried to use ΔE as a measure of the cation stabilization effect for TTF, BEDO, and BEDT. Intuitively, the voltage separation between the first and second oxidation steps should depend upon how well the mono- and particularly the di-cationic species are stabilized by the medium. Figure 2 demonstrates the validity of this approach. Remarkably linear correlations exist between the ΔE values for all three compounds. Plots of ΔE for BEDT and TTF *vs.* ΔE for BEDO have nearly identical slopes. It seems therefore, not surprisingly, that the oxidation processes of all three compounds have essentially the same medium dependence. Interestingly, ΔE's for BEDO and BEDT were found to be virtually identical in all solvents.

The remarkably good correlations of Figure 2 justify the use of ΔE of each of the compounds as a reasonable measure of the cation stabilization (CS) effect of the corresponding solvent. Figure 3 shows a plot of $\Delta E1$ *vs.* the newly defined specific cation solvation parameter, CS (ΔE for BEDO). Despite some scatter, the correlation is excellent when compared to the plots in Figure 1. The negative slope unequivocally reveals that, although still larger, the first oxidation potential for BEDO approaches that of TTF as the stabilizing power of the solvent/electrolyte system (expressed as CS) decreases. This can be taken as strong evidence for the medium facilitated oxidation of TTF relative to BEDO. Furthermore, on conceptual extrapolation of the line in Figure 3 to the gas phase where solvation is nonexistent and where ΔE (or better IP2 − IP1) is very large, the sign of $\Delta E1$ becomes negative, *i.e.*, the ionization potential (IP) of BEDO is lower than that of TTF, in good agreement with results of UVPES.[2]

Not surprisingly, the environmental parameter CS is only applicable to members of a particular family of donors, in this case the thiafulvenoid donors. As can be seen from Figure 4, $\Delta E1$ [$E1$ (TMPD) − $E1$ (TTF)] of tetramethyl-*p*-phenylenediamine (TMPD) shows poor correlation with CS. We conclude that CS reflects specific molecular cation–milieu interactions. Also in accord with intuition, there is a good linear correlation ($R = 0.962$) between CS and solvent donicity numbers as shown in Figure 5. That there is a poorer correlation between $\Delta E1$ and DN (Figure 5B) than between $\Delta E1$ and CS is further indication that CS is a better measure of relative cation stabilization than DN.

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